

# Ambipolar Phosphorene Field Effect Transistor

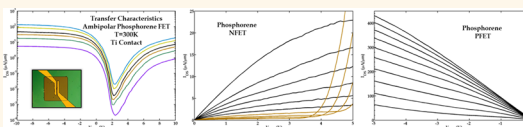
Saptarshi Das,<sup>\*,†,‡</sup> Marcel Demarteau,<sup>‡</sup> and Andreas Roelofs<sup>†</sup>

<sup>†</sup>Center for Nanoscale Material and <sup>‡</sup>Division of High Energy Physics, Argonne National Laboratory, Argonne, Illinois 60439, United States

**ABSTRACT** In this article, we demonstrate enhanced electron and hole transport in few-layer phosphorene field effect transistors (FETs) using titanium as the source/drain contact electrode and 20 nm SiO<sub>2</sub> as the back gate dielectric.

The field effect mobility values were extracted to be  $\sim 38$  cm<sup>2</sup>/Vs for electrons and

$\sim 172$  cm<sup>2</sup>/Vs for the holes. On the basis of our experimental data, we also comprehensively discuss how the contact resistances arising due to the Schottky barriers at the source and the drain end effect the different regime of the device characteristics and ultimately limit the ON state performance. We also propose and implement a novel technique for extracting the transport gap as well as the Schottky barrier height at the metal–phosphorene contact interface from the ambipolar transfer characteristics of the phosphorene FETs. This robust technique is applicable to any ultrathin body semiconductor which demonstrates symmetric ambipolar conduction. Finally, we demonstrate a high gain, high noise margin, chemical doping free, and fully complementary logic inverter based on ambipolar phosphorene FETs.



**KEYWORDS:** phosphorene · ambipolar field effect transistor · contact resistance · logic inverter

Two-dimensional layered materials are being actively investigated as an alternative to silicon for future generations of nanoelectronic devices due to their ultrathin body, which enables efficient electrostatic gate control when used in field effect transistor geometry. Pioneering work started with groundbreaking experiments regarding graphene, a monolayer of hexagonally arranged carbon atoms, by Novoselov and Geim.<sup>1,2</sup> Graphene has extremely high carrier mobility ( $\sim 20\,000$  cm<sup>2</sup>/Vs at room temperature) and the potential to reach ballistic transport at relatively large length scales; however, the absence of a finite band gap imposes severe challenges on its implementation into logic transistors which require large (at least 4 orders of magnitude) current ON/OFF ratios. A considerable effort is being dedicated to manufacturing a band gap in graphene through size quantization in nanoribbons and the electric field in bilayers.<sup>3,4</sup> Semiconducting transition metal dichalcogenides (TMDs), on the contrary, possess a finite and tunable band gap that can range from  $\sim 0.4$  to  $\sim 2.3$  eV but at the expense of low carrier mobility. Field effect transistors (FETs) fabricated on molybdenum- and tungsten-based sulfides, selenides, and tellurides have demonstrated more than 6–7 orders of magnitude current ON/OFF ratios and excellent subthreshold swings (close to an

ideal value of 60 mV/decade) but with mobility values ranging from 10 to 200 cm<sup>2</sup>/Vs.<sup>5–15</sup> It is important to mention here that, in the context of aggressive channel length scaling, the low mobility values of the TMDs do not invoke any concern because, for technology nodes beyond 10 nm, the transport mechanism in the semiconducting channel of the transistor will be dominated by ballistic processes instead of scattering.<sup>16–19</sup> However, there are many other applications like the RF transistors and thin film transistors, where high mobility is extremely desirable for high performance. Phosphorene, the youngest member (by the chronology of its discovery) of this exotic class of two-dimensional crystals, is capturing a lot of attention since in addition to a finite band gap (that can range from 0.3 eV in bulk to 1.0 eV in monolayers) it also possesses high carrier mobility of  $\sim 1000$  cm<sup>2</sup>/Vs for the hole transport.<sup>19–23</sup> What could potentially limit the application of phosphorene is the electron transport which so far has not been demonstrated. The availabilities of both the electrons in the conduction band and the holes in the valence band are essential features for not only complementary logic designs but also other applications. In this article, we show by tuning the work function of the contact metal and by scaling the thickness of the gate oxide that electron transport can indeed be realized in phosphorene. We report

\* Address correspondence to [das.sapt@gmail.com](mailto:das.sapt@gmail.com), [das@anl.gov](mailto:das@anl.gov).

Received for review September 11, 2014 and accepted October 20, 2014.

Published online October 20, 2014  
10.1021/nn505868h

© 2014 American Chemical Society

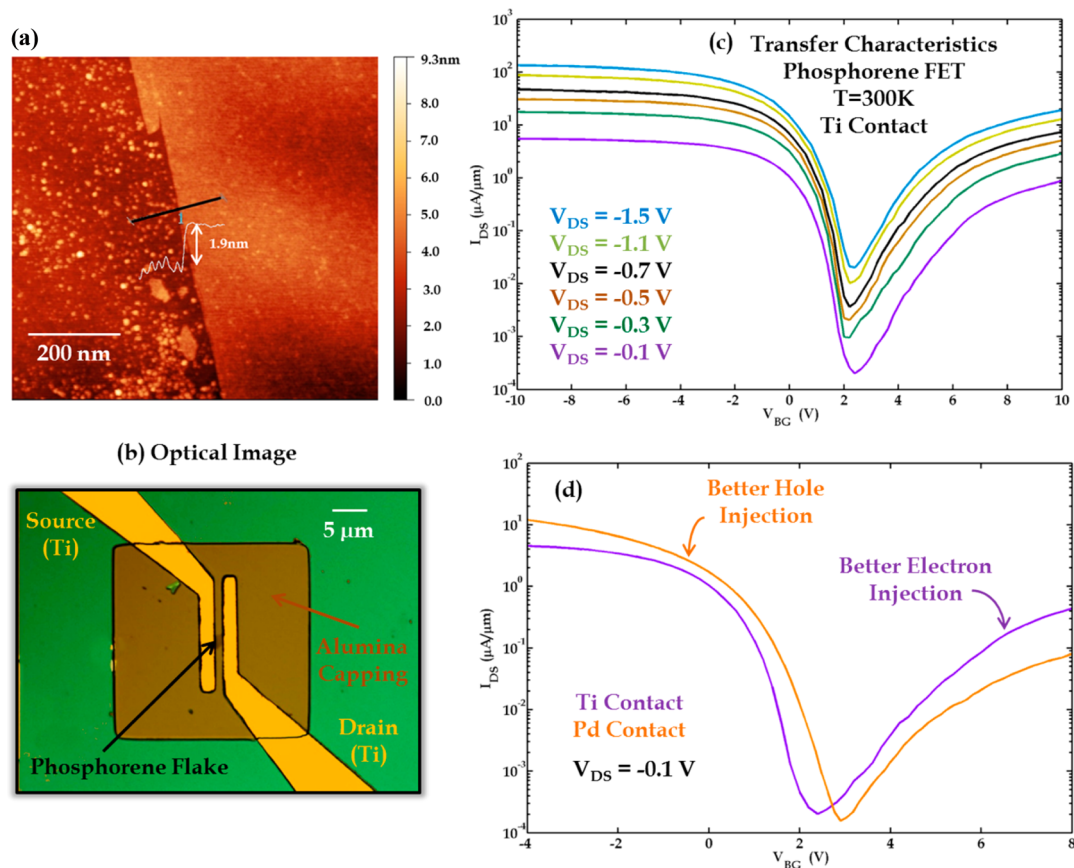


Figure 1. (a) AFM image of a 1.9 nm thick phosphorene flake with a 10 nm capping layer of alumina deposited using e-beam evaporation immediately after exfoliation in order to prevent degradation due to atmosphere. (b) Optical image of a prototype device with a 60 nm capping layer of alumina. (c) Room temperature transfer characteristics in logarithmic scale for different source to drain biases ( $V_{DS}$ ) of a back-gated phosphorene FET with Ti as the source/drain contacts. (d) Transfer characteristics of phosphorene FETs with Ti and Pd contact.

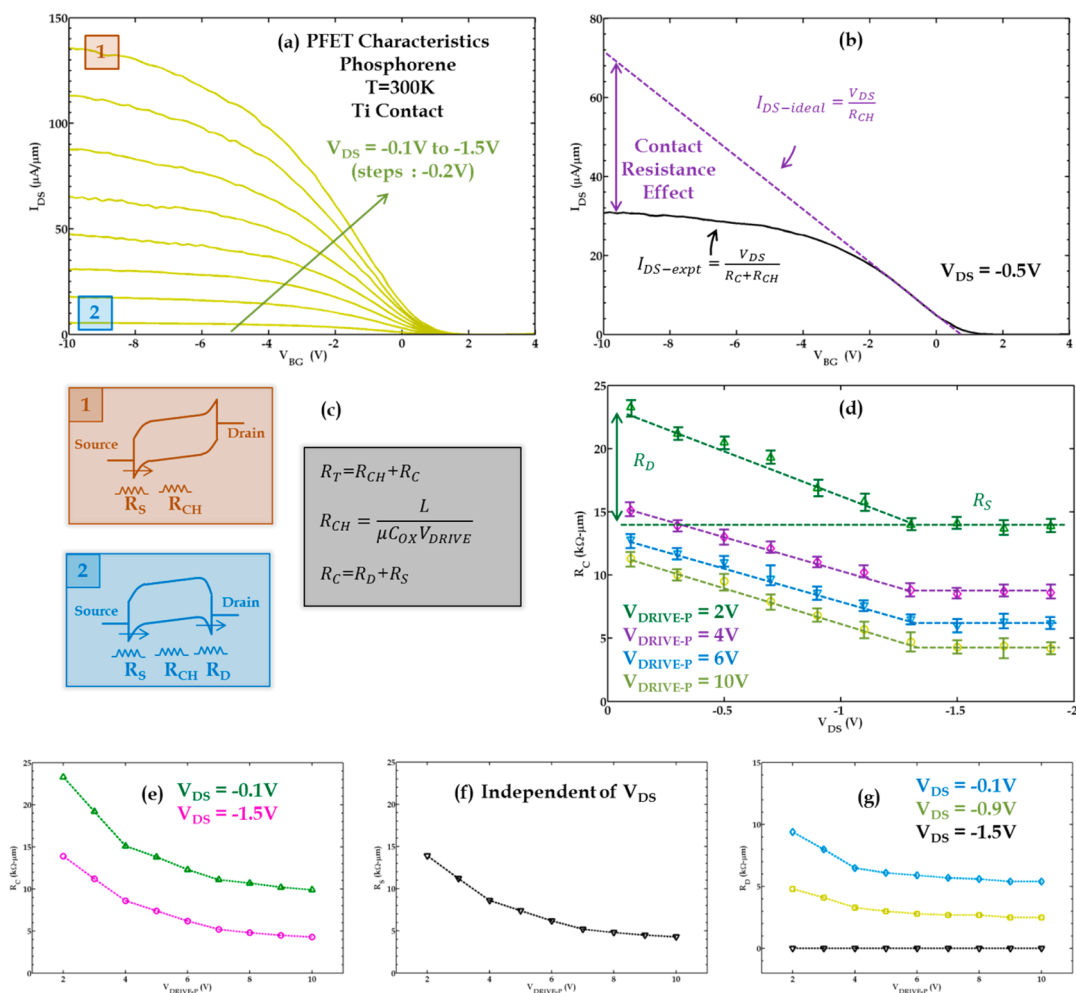
record high electron field effect mobility of  $\sim 38$  cm<sup>2</sup>/Vs in phosphorene. Our hole field effect mobility of  $\sim 172$  cm<sup>2</sup>/Vs is also consistent with the earlier findings.<sup>19–23</sup>

One of the major concerns for high mobility transistors based on low-dimensional materials in general is the nonscalability of contact resistance. Note that in the absence of a controllable and sustainable substitutional doping scheme, one has to rely on the work function of contact metals to inject appropriate types of carriers into the respective bands of these two-dimensional semiconductors.<sup>10,25,26</sup> Such metal semiconductor contacts are almost always associated with finite Schottky barrier heights. The phenomenon of Fermi level pinning,<sup>6,17,27</sup> makes the situation even more challenging since the alignment of the metal Fermi level with the bands of the semiconducting channel is no longer determined by the work function of the contact metal. In this article, we, therefore, extract the different components of such a Schottky barrier contact resistance from our experimental device characteristics and then discuss how the different regime of device operation is affected by those. In this context, we also propose and implement a novel

technique for determining the Schottky barrier height at a metal to semiconductor interface from the transfer characteristics of an ambipolar Schottky barrier field effect transistor (SBFET). This technique is further extended to determine the transport gap of the semiconducting channel material, which in our case is phosphorene. Finally, we employed electrostatic doping to combine a high-performance phosphorene p-type field effect transistor (PFET) with a phosphorene n-type field effect transistor (NFET) in a double-gated transistor geometry to demonstrate a fully complementary logic inverter. The maximum gain of our chemical doping free phosphorene inverter was found to be  $\sim 8$ , and the noise margin was close to its ideal value of  $\sim 2.5$  V for a supply voltage of  $V_{DD} = 5.0$  V.

## RESULTS

Figure 1a shows the AFM image of a 1.9 nm thick flake with the Al<sub>2</sub>O<sub>3</sub> capping layer on top. Figure 1b shows the optical image of a prototype device gated from the back. The use of 20 nm thick SiO<sub>2</sub> compared to conventionally used 300 nm thick SiO<sub>2</sub> was motivated by the fact that scaled oxide reduces the Schottky barrier tunneling distance and thereby improves the

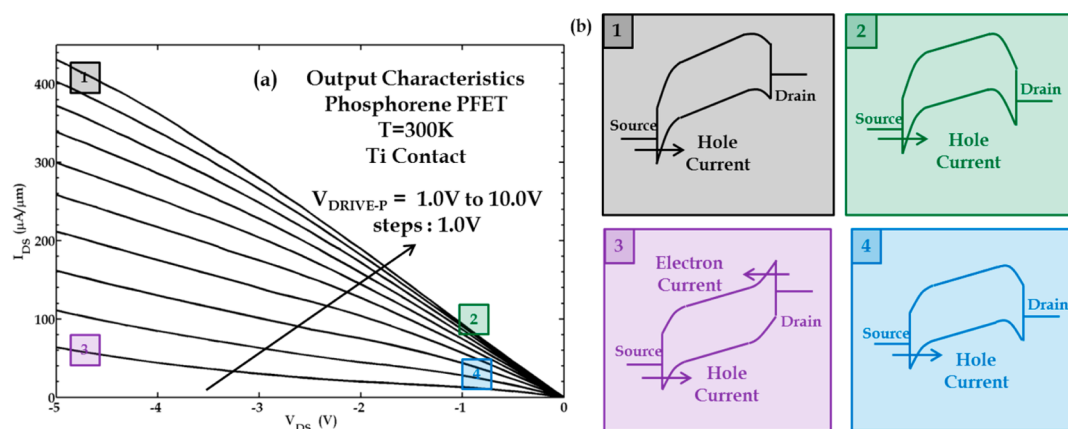


**Figure 2.** (a) Transfer characteristics (in linear scale) of phosphorene PFET. (b) Demonstration of the model for extracting the contact resistance ( $R_C$ ) from the device characteristics. (c) Band diagrams and associated resistances for different transport regimes. (d) Different components of contact resistance extracted using panel b at different  $V_{\text{DRIVE-P}}$  values and their dependence on the applied  $V_{\text{DS}}$ . The dependence of (e)  $R_C$ , (f)  $R_S$ , and (g)  $R_D$  on the back gate bias.

carrier injection.<sup>28,29</sup> The channel length of the device was  $\sim 2 \mu\text{m}$ . Figure 1c shows the transfer characteristics of this phosphorene FET for different negative drain biases ( $V_{\text{DS}}$ ) at room temperature in logarithmic scale. Clearly, both electron and hole conduction are observed. The ON/OFF current ratios were found to be  $\sim 2.7 \times 10^4$  for the hole conduction and  $\sim 4.4 \times 10^3$  for electron conduction, which suggests that the Fermi level of Ti is aligned close to the middle of the band gap of phosphorene with a slight shift toward the valence band. Figure 1d shows the transfer characteristics of phosphorene FETs with similar flake thicknesses as Ti and Pd contacts. Both devices have a 60 nm capping layer of  $\text{Al}_2\text{O}_3$ . The fact that the Ti contact device exhibits a more pronounced electron branch compared to the Pd contact device suggests that Ti provides a smaller Schottky barrier height for electron injection into phosphorene.

Figure 2a shows the transfer characteristics of the same phosphorene FET for negative source to drain biases ( $V_{\text{DS}}$ ) and negative back gate biases ( $V_{\text{BG}}$ ) in

linear scale. These bias conditions electrostatically dope the phosphorene with holes which results in PFET device characteristics. The field effect mobility for the hole conduction was extracted from the peak transconductance value using the conventional equation for  $g_m = \mu_p C_{\text{OX}}(W/L)V_{\text{DS}}$  (where  $g_m$  is the transconductance,  $\mu_p$  is the field effect mobility for the holes, and  $W$  and  $L$  are the channel width and the channel length, respectively;  $C_{\text{OX}} = \epsilon_{\text{OX}}/d_{\text{OX}}$ , where  $\epsilon_{\text{OX}}$  is the dielectric constant and  $d_{\text{OX}}$  is the thickness of the gate oxide;  $d_{\text{OX}} = 20 \text{ nm}$ , and for  $\text{SiO}_2$ ,  $\epsilon_{\text{OX}} = 3.5 \times 10^{-11} \text{ F/m}$ , which gives  $C_{\text{OX}} \sim 1.7 \times 10^{-3} \text{ F/m}^2$  and finally  $L \sim 2 \mu\text{m}$ ) and was found to be  $\sim 172 \text{ cm}^2/\text{Vs}$ . It is interesting to note that the  $I_{\text{DS}}$  versus  $V_{\text{BG}}$  curves for any given  $V_{\text{DS}}$  saturate for large overdrive voltages ( $V_{\text{DRIVE-P}} = |V_{\text{BG}} - V_{\text{TH-P}}|$ , where  $V_{\text{TH-P}}$  is the threshold voltage for the hole conduction). This saturation is a result of contact resistance limiting the current flow through the phosphorene channel. In order to account for this contact resistance, we use the simple fact that the total resistance ( $R_T$ ) of the phosphorene FET can be written as



**Figure 3.** (a) Output characteristics and (b) associated band diagrams for different regimes of device operation for phosphorene PFET.

$R_T = R_C + R_{CH}$ , where  $R_C$  is the contact resistance and  $R_{CH}$  is the channel resistance. The dependence of channel resistance on the applied back gate bias in the linear region of the device characteristics is given by  $R_{CH} = L/\mu_p C_{OX} V_{DRIVE-P}$ . The reader should note that the charge carrier density in the electrostatically doped phosphorene channel reaches  $Q_{GATE} = 10^{13}/\text{cm}^2$  for a gate overdrive voltage of  $V_{DRIVE-P} = 10$  V. At this high carrier concentration, the mobility may be impacted through scattering processes. In fact, in our earlier article,<sup>22</sup> we found that the carrier mobility follows a power law dependence on the carrier concentration ( $\mu \propto Q_{GATE}^\gamma$ ) with  $\gamma = -0.16$  for bilayer phosphorene. This certainly needs to be taken into account for more accurate extraction of the contact resistance. The modified equations are as follows.

$$\mu_p = \mu_{PO} V_{DRIVE-P}^\gamma$$

$$R_{CH} = \frac{1}{\mu_{PO} C_{OX} V_{DRIVE-P}^{1+\gamma}}$$

Note that the current and resistance values are normalized to the width. In Figure 2b, the solid black curve shows the measured current as a function of the applied back gate bias for  $V_{DS} = -0.5$  V, and the dotted purple line shows the ideal case scenario without any contact resistance. Note that the dotted line is a fit to the linear portion of the  $I_{DS}$  versus  $V_{BG}$  curve with  $V_{TH} = 0.7$  V and  $\mu_p = 172$   $\text{cm}^2/\text{Vs}$ . The channel resistance value was found to be  $6.7$   $\text{k}\Omega \cdot \mu\text{m}$  for  $V_{DRIVE} = 10$  V. Figure 2d shows that the extracted contact resistance decreases monotonically with the applied source to drain bias ( $V_{DS}$ ) and finally plateaus at a lower value (for any given overdrive voltage  $V_{DRIVE-P}$ ). The reader should note that the contact resistance  $R_C$  is the sum of the individual contact resistances at the source ( $R_S$ ) and drain ( $R_D$ ) ends due to the respective Schottky barriers, as shown in Figure 2c. For small  $V_{DS}$  in a long channel device, the channel potential at the source end is completely determined by  $V_{BG}$ , ensuring that both the height

and the width of the Schottky barrier remain unchanged. The source contact resistance, therefore, remains constant as a function of the applied  $V_{DS}$ . The drain contact resistance  $R_D$  resulting from the Schottky barrier at the drain end, however, changes with the applied  $V_{DS}$  as the Schottky barrier height is monotonically reduced and finally eliminated, as shown in Figure 2c. For  $V_{DRIVE-P} = 2.0$  V,  $R_S$  was found to be  $13.7$   $\text{k}\Omega \cdot \mu\text{m}$ , and for small  $V_{DS}$  and  $R_S$ , it was found to be  $9.9$   $\text{k}\Omega \cdot \mu\text{m}$ . This is consistent with the fact that for small  $V_{DS}$  the Schottky barriers at the source and the drain ends are almost symmetric, and therefore, the contact resistances should be very similar. The dependence of  $R_C$ ,  $R_S$ , and  $R_D$  as a function of the gate bias is shown in Figure 2e–g, respectively. As expected,  $R_S$  decreases monotonically with increasing  $V_{DRIVE-P}$  due to the combined effect of a reduced Schottky barrier tunneling distance and electrostatic doping of phosphorene underneath the source contact.  $R_D$  also shows a similar trend for small  $V_{DS}$  values since the Schottky barrier at the drain end influences the current conduction. The combined effect is reflected in the total contact resistance  $R_C$ . Note that similar findings have been reported for Pd and Ni contacts to phosphorene by Du *et al.*<sup>24</sup> using a channel length scaling study. Using the data from ref 24 and data presented in this article, the contact resistance values for Pd, Ni, and Ti contacted phosphorene are found to be  $1.75$ ,  $3.15$  and  $4.85$   $\text{k}\Omega \cdot \mu\text{m}$ , respectively, for large gate bias and drain bias conditions. This is consistent with the fact that smaller work function metals give rise to larger Schottky barrier heights for the hole injection into the valence band, resulting in larger contact resistance values. The phenomenon of Fermi level pinning is present at the metal to phosphorene interface because both large work function Pd and low work function Ti contacts resulted in better hole conduction.<sup>6,27</sup>

Figure 3a shows the room temperature output characteristics of the phosphorene PFET for different

values of  $V_{\text{DRIVE-P}}$ . For large  $V_{\text{DRIVE-P}}$  values, the band positions in the channel are depicted in the black and the green semitransparent boxes in Figure 3b corresponding to high and low  $V_{\text{DS}}$  values, respectively (points 1 and 2 in Figure 3a). As evident, these bias conditions are conducive for hole injection into the valence band *via* tunneling through the Schottky barrier. Electron injection into the conduction band, on the contrary, is limited due to the existence of large thermal barriers. In this context, it is important to mention that the linear nature of our  $I_{\text{DS}}$  *versus*  $V_{\text{DS}}$  characteristics should not be interpreted as the result of an Ohmic contact.<sup>6</sup> As comprehensively discussed in our earlier articles, the linear nature of output characteristics could be a result of either a small Schottky barrier height smeared out due to thermal broadening of the Fermi function or reduced Schottky barrier tunneling distance due to scaled oxide, scaled body thickness, or large  $V_{\text{DRIVE}}$ . In ultrathin phosphorene FETs on 20 nm  $\text{SiO}_2$ , we are, therefore, expected to observe linear  $I_{\text{DS}}$  *versus*  $V_{\text{DS}}$  characteristics. For small  $V_{\text{DRIVE}}$  values, the situation is more interesting. As the applied  $V_{\text{DS}}$  is increased, the Schottky barrier height at the drain end is reduced, and this results in a monotonic increase in the hole conduction current before it saturates, as shown in the band diagram in the blue semitransparent box in Figure 3b (point 4 in Figure 3a). The magnitude of the current in the saturation regime is controlled by the gate bias which determines the position of the bands in the channel. As the  $V_{\text{DS}}$  is increased beyond the saturation regime, the current again starts to increase because the band bending situation at the drain end becomes conducive for electrons to tunnel (through the Schottky barrier) into the conduction band, as shown in the purple semitransparent box in Figure 3b (point 3 in Figure 3a). This is another clear evidence of typical ambipolar behavior of a semiconducting channel material. Please note that in the ON state of the device characteristics, that is, above the threshold, the energy bands ( $\Psi_s$ ) in the semiconducting channel of a FET do not respond in a 1:1 way to the applied gate overdrive voltage ( $V_{\text{DRIVE-P}}$ ). This is because the channel capacitance (also referred to as the quantum capacitance  $C_Q$ ) becomes significantly larger compared to the gate oxide capacitance.<sup>30,31</sup> In fact, it is given by the following equation:

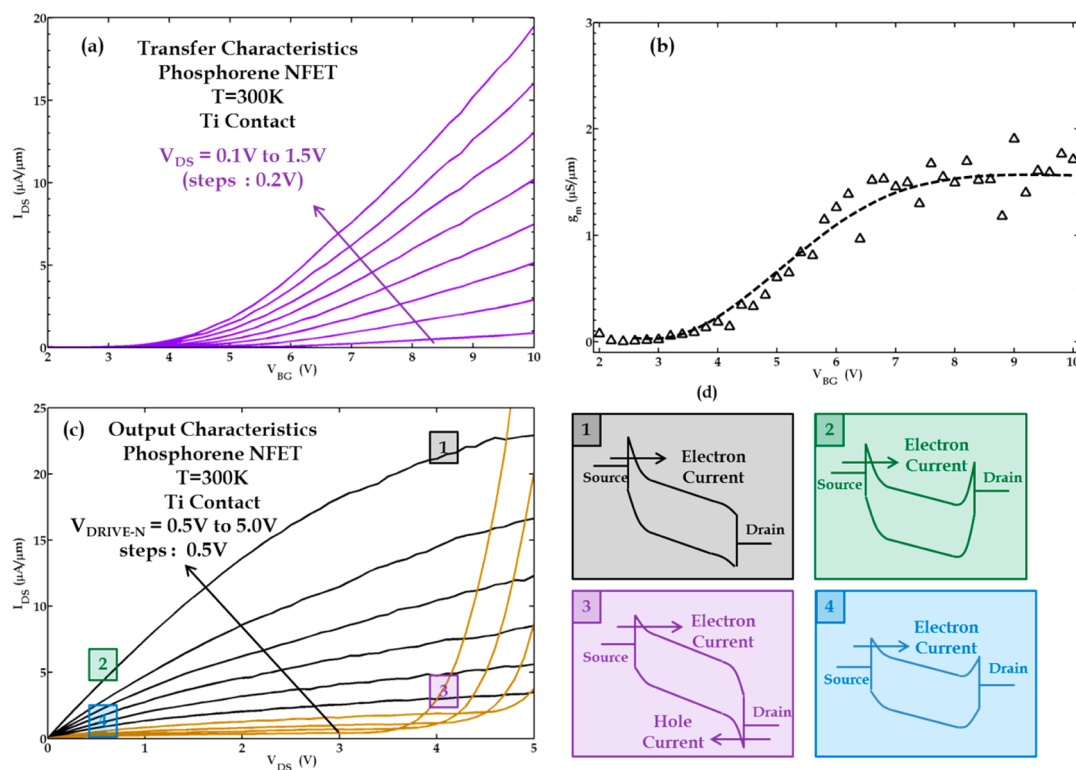
$$d\Psi_s = \frac{C_{\text{OX}}}{C_{\text{OX}} + C_Q} dV_{\text{DRIVE-P}}$$

The threshold condition for hole conduction (for negative drain bias case) is generally reached when the valence band in the channel of the transistor aligns with the metal Fermi level at the source end. The band movement becomes increasingly slow as  $C_Q$ , which is proportional to the 2D density of states, increases monotonically for gate overdrive voltages ( $V_{\text{DRIVE-P}}$ ) beyond the threshold.<sup>31,32</sup> Moreover, in the ON state

of a Schottky barrier FET, most of the drain potential drops across the contacts.<sup>30</sup> Therefore, the slope of the valence band is similar to what has been depicted in Figure 3b. Additionally, in a long channel device (which is indeed the case for our phosphorene FETs), the gate is in firm control of the bands in the channel. All this would justify the drawing of our qualitative band diagrams and hence the explanation given for the current increase in the saturation region at low gate bias.

Figure 4a shows the transfer characteristics of the same phosphorene FET for positive source to drain biases ( $V_{\text{DS}}$ ) and positive back gate biases ( $V_{\text{BG}}$ ). These bias conditions electrostatically dope the phosphorene with electrons, which results in NFET device characteristics. Figure 4b shows the transconductance ( $g_m$ ) for the electron transport as a function of  $V_{\text{BG}}$ . Note that the transconductance plateaus at the maximum value, which suggests that the contact resistance does not affect the electron conduction. This can also be substantiated by the fact that the channel resistance ( $R_{\text{CH}}$ ) for the electron transport even for  $V_{\text{DRIVE}} = 10$  V is  $\sim 75.4$   $\text{k}\Omega \cdot \mu\text{m}$ , which is much higher than the contact resistance of  $R_C \sim 10$   $\text{k}\Omega \cdot \mu\text{m}$  ( $R_D + R_S$ ). The reader might question the validity of using the same contact resistance value for both electron and hole transport since the Schottky barrier height for electron and hole injection could be very different. However, as we will deduce later, the Fermi level of Ti was found to be aligned to the middle of the band gap of phosphorene, which results in similar Schottky barrier heights for electron and hole injection, and therefore, the contact resistances are indeed the same. The field effect mobility for the electron transport, extracted from the plateau in  $g_m$ , was found to be  $38$   $\text{cm}^2/\text{Vs}$ . This is the highest reported electron mobility in phosphorene. Figure 4c shows the room temperature output characteristics of the phosphorene NFET for different values of  $V_{\text{DRIVE}}$ , and Figure 4d shows the associated band positions. The device characteristics corresponding to the electron transport can be explained using the exact same analogy described for the hole transport. Large  $V_{\text{DRIVE}}$  values facilitate only electron transport (the green and black semitransparent boxes in Figure 4d), while small  $V_{\text{DRIVE}}$  values coupled with large  $V_{\text{DS}}$  values enable hole tunneling current in addition to the already existing electron current (purple semitransparent box in Figure 4d). Since the hole mobility is  $\sim 5$  times higher than the electron mobility, the impact is much more pronounced (as seen in the gold plots in Figure 4c) than what is observed in the output characteristics associated with the PFET.

Now we would like to justify the claim made earlier regarding the alignment of the Ti Fermi level with the energy bands of phosphorene. In this context, we report an innovative way of extracting the Schottky barrier height and the transport gap of a semiconductor from the transfer characteristics of a FET. Note that

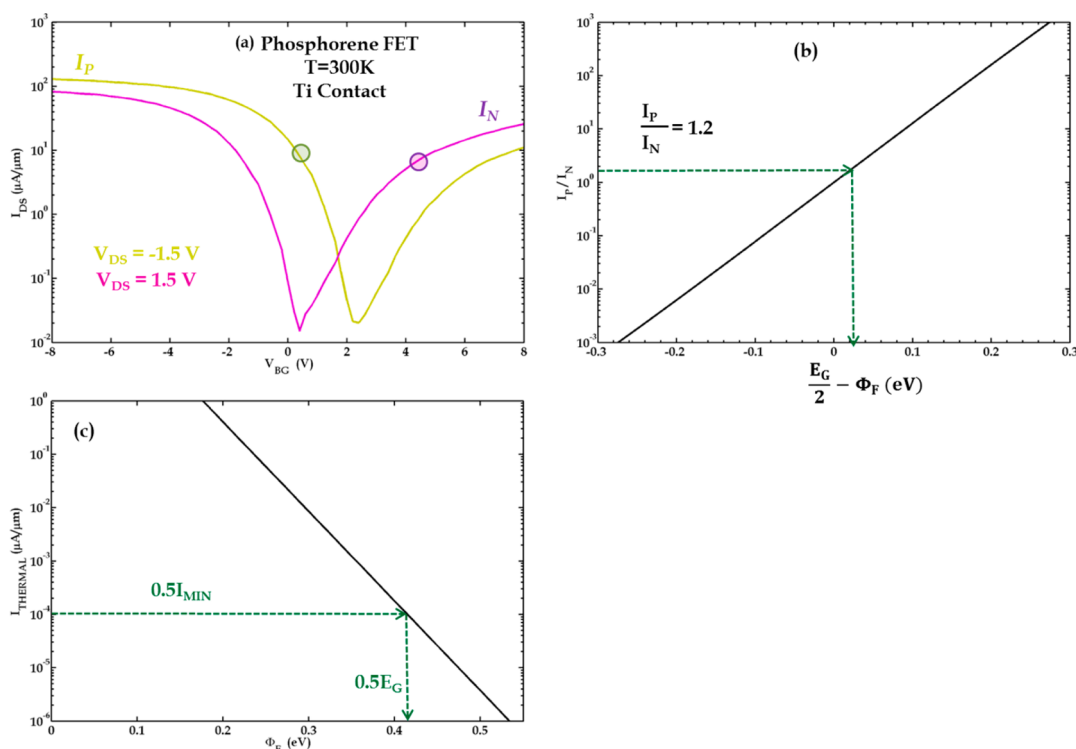


**Figure 4.** (a) Transfer characteristics (in linear scale) of n-type phosphorene FET. (b) Transconductance as a function of the back gate bias. (c) Output characteristics and (d) associated energy band diagrams for different transport regimes. The gold curves in panel c show how the hole conduction becomes pronounced for large drain biases for small  $V_{DRIVE-N}$ .

we will refer to the extracted band gap as the “transport gap” in the context of current transport. This is because the presence of surface states and unaccounted gap states can influence the current conduction in a semiconductor to a considerable extent and hence manifest in an effective band gap. Figure 5a shows the logarithmic plot of  $I_{DS}$  versus  $V_{BG}$  for large positive and negative drain biases. We have used  $V_{DS} = 1.5$  V in order to determine the electron current  $I_N$  (marked by the purple semitransparent dot) and  $V_{DS} = -1.5$  V in order to determine the hole current  $I_P$  (marked by the green semitransparent dot) at their corresponding threshold voltages. The threshold voltages ( $V_{TH-N} = V_{BG} = 4.5$  V and  $V_{TH-P} = V_{BG} = 0.5$  V) were extracted from the linear  $I_{DS}$  versus  $V_{BG}$  plots shown in Figures 2a and 4a. Since the magnitudes of  $I_P$  and  $I_N$  are determined by the respective Schottky barrier heights for the electron and hole injection, the ratio of  $I_P$  and  $I_N$  is a direct measure of the alignment of the metal Fermi level with the electronic bands of the phosphorene. The reader should note that for a Schottky barrier device the current at the threshold is limited by tunneling through the Schottky barrier rather than scattering in the channel due to a small number of charge carriers. Figure 5b shows the simulated ratio of hole conduction current to electron conduction current at threshold as a function of the alignment of the metal Fermi level with the middle of the band gap. For perfect mid-gap alignment, the electron and hole

conduction currents must be equal with the ratio being equal to 1. The  $I_P/I_N$  ratio extracted from Figure 5a was found to be  $\sim 1.2$ . Note that the exponential dependence of the ratio of electron to hole current ( $I_N/I_P$ ) on the relative position of the SB height (Figure 5b) makes this technique considerably robust. As seen in Figure 5c, even an order of magnitude error in the determination of  $I_N/I_P$  results in a corresponding error of 50 meV in the extraction of the SB height. So within these error bars and based on the above analysis, it is justified to assume that, for Ti contacts to phosphorene,  $E_G = 2\Phi_F$ .

We will now use this fact to extract the transport gap of phosphorene. If we focus on the minimum current point ( $I_{MIN}$ ) of the device characteristics, we immediately realize that  $I_{MIN}$  is the superposition of two equal components: the thermionic hole emission current ( $I_P = 0.5I_{MIN}$ ) injected from the source and the thermionic electron emission current ( $I_N = 0.5I_{MIN}$ ) injected from the drain. Figure 5c shows the thermionic emission current calculated as a function of the barrier height using the Landauer formalism and assuming ballistic transport.<sup>20,21</sup> This assumption is justified since in the OFF state of the device characteristic scattering in the channel is negligible due to the absence of a sufficient number of charge carriers. In our phosphorene FETs, at the minimum current point,  $I_N = I_P = 10^{-4} \mu A/\mu m$ , which corresponds to  $\Phi_F = 0.43$  eV and hence  $E_G = 0.86$  eV. According to the photoluminescent data and DFT simulations, this band gap would

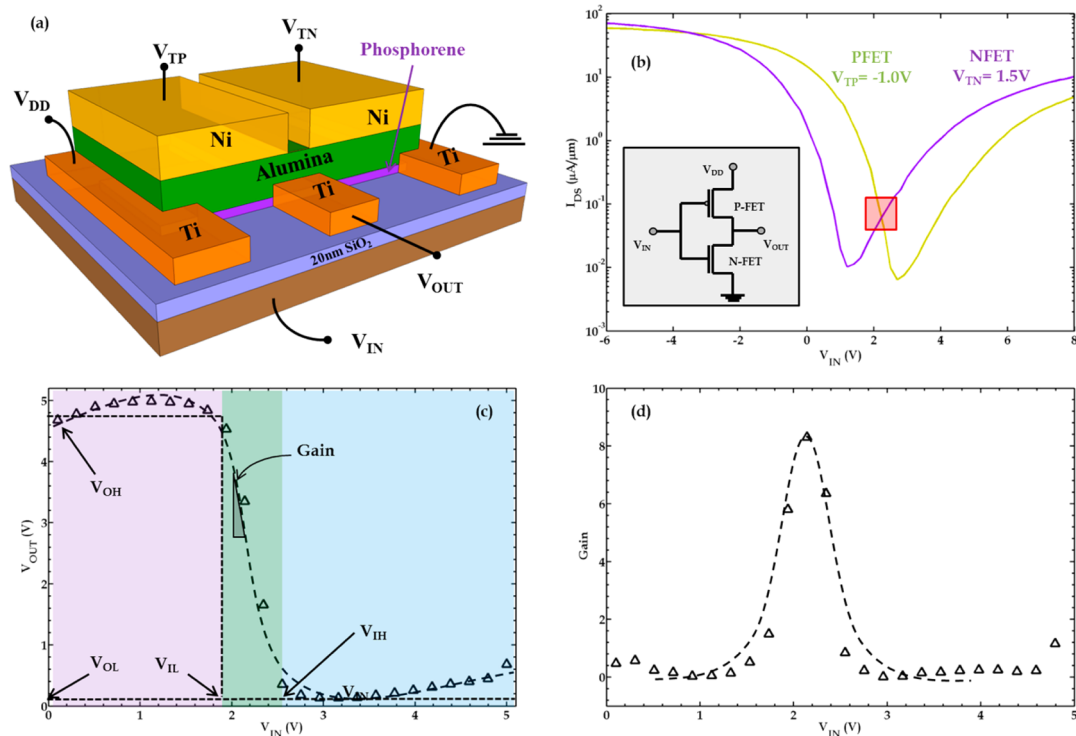


**Figure 5.** (a) Transfer characteristics of bilayer phosphorene FET for positive and negative  $V_{DS}$ .  $I_P$  and  $I_N$  are extracted for the same gate overdrive voltages  $V_{DRIVE-N} = V_{DRIVE-P}$ . (b) Simulated ratio of hole conduction current to electron conduction current for different positions of the contact Fermi level with respect to the energy bands of the phosphorene. The ratio of  $I_N/I_P$  is plotted after correcting for the different mobility values of the electron and the hole carriers. (c) Simulated thermionic current for different barrier heights.

correspond to a flake thickness in the range of 3–5 layers.<sup>33</sup> We would like to clarify that this innovative technique of extracting the Schottky barrier and the band gap of a semiconducting channel material can only be applied when the device characteristics are relatively symmetric (the magnitudes of  $I_N$  and  $I_P$  do not differ by more than an order of magnitude). This is indeed the case with phosphorene FETs contacted by titanium.

Finally, we demonstrate a fully complementary logic inverter based on ambipolar phosphorene FETs. Figure 6a shows the 3D cartoon projection merged on top of an optical image of a phosphorene inverter fabricated on a single flake.  $V_{IN}$  (which is equivalent to  $V_{BG}$ ) is the input voltage;  $V_{OUT}$  is the output voltage, and  $V_{TP}$  and  $V_{TN}$  are the top gate voltages applied to the phosphorene flake in order to electrostatically dope it with p-type and n-type carriers, respectively. The 60 nm alumina ( $\text{Al}_2\text{O}_3$ ) was used as the top gate dielectric, and Ni was used as the top gate electrode for both the PFET and the NFET. Negative top gate voltages ( $V_{TP}$ ) are used to electrostatically dope the phosphorene flakes with holes, and positive top gate voltages ( $V_{TN}$ ) are used to electrostatically dope the phosphorene flakes with electrons. What essentially happens is that the top gate voltage changes the position of the energy bands in the semiconducting channel, and that results in a corresponding threshold voltage shift. The shift in the threshold voltage ( $\Delta V_{TH}$ )

can be calculated from the principal of charge balance:  $C_{TG} \cdot \Delta V = C_{BG} \cdot \Delta V_{TH}$ , where  $C_{TG}$  and  $C_{BG}$  are the capacitances associated with the top and the back gates, respectively, and  $\Delta V$  is the change in the top gate bias. In our experiment,  $C_{TG} = 1.2 \times 10^{-3} \text{ F/m}^2$  and  $C_{BG} = 1.7 \times 10^{-3} \text{ F/m}^2$ , which results in a  $\sim 2.0 \text{ V}$  shift in threshold voltage for every 3.0 V change in the  $V_{TP}$  or  $V_{TN}$ . Figure 6b shows the transfer characteristics of the PFET and the NFET as a function of the input voltage  $V_{IN}$  ( $V_{BG}$ ) for  $V_{TP} = -1.0 \text{ V}$  and  $V_{TN} = 1.5 \text{ V}$ , respectively. Figure 6c shows the complementary inverter characteristics based on our double-gated phosphorene FET. There are three essential regions in the inverter characteristics: the region where the input voltage ( $V_{IN}$ ) is relatively low, so that the output voltage ( $V_{OUT}$ ) is high (shown in purple); the region where the input voltage ( $V_{IN}$ ) is relatively high, so that the output voltage ( $V_{OUT}$ ) is low (shown in blue); and finally, the transition region, where the input/output voltages are in an indeterminate state (an ambiguous region between high and low shown in green). The transition region is defined as the region where the gain ( $G$ ) of the inverter is more than 1. Note that the gain ( $G$ ) is the slope of the inverter characteristics; that is,  $G = dV_{OUT}/dV_{IN}$ . An ideal inverter should have infinite gain, which eliminates the transition region. Figure 6d shows the gain of our fully complementary bilayer phosphorene inverter as function on  $V_{IN}$ . The maximum gain was found to be 8.



**Figure 6.** (a) Three-dimensional cartoon of a double-gated phosphorene FET structure used for the logic inverter. (b) Transfer characteristics of phosphorene PFET and phosphorene NFET realized through electrostatic doping. (c) Transfer characteristics of phosphorene logic inverter. (d) Gain of the inverter as a function of the input voltage.

The gain of the inverter is the highest when the intersection of the PFET and NFET transfer characteristics occurs in the steepest portion of their subthreshold behavior. This is very obvious since a steeper subthreshold swing signifies rapid changes in the corresponding current levels and hence abrupt transition from the PFET to the NFET and *vice versa*. The low gain in our inverter, therefore, can be explained from the fact that the subthreshold slopes of our PFET and NFET at the cross-over point (marked by the red box in Figure 6b) are  $\sim 0.6$  V/decade, which is 10 times worse than the ideal achievable slope of 60 mV/decade.

Noise margin (NM) is another important parameter in the context of the inverter which determines how stable the output is with respect to signal interference at the input. As shown in Figure 6c, the input voltage is considered to be at logic high ("1") if  $V_{IN} > V_{IH}$  and at logic low ("0") if  $V_{IN} < V_{IL}$ . This is because input voltages in these ranges can produce unambiguous output logic levels.  $V_{OH}$  and  $V_{OL}$  are, respectively, the ideal logic high and logic low of the inverter. Noise margins for high input ( $NM_H$ ) and noise margins for low input ( $NM_L$ ) are, therefore, defined as  $NM_H = V_{OH} - V_{IH}$  and

$NM_L = V_{IL} - V_{OL}$ . For a supply voltage of  $V_{DD} = 5.0$  V, we obtained a nearly ideal noise margin of  $\sim 2.25$  V for the high input and 1.85 V for the low input. We would like to remind the reader that the inverter characteristics could be strongly impacted if there is hysteresis in the device characteristics. Our back-gated phosphorene devices show a hysteresis of  $\sim 200$  meV, which is considerably low and does not influence the inverter operation (see Supporting Information).

## CONCLUSION

In conclusion, we have successfully demonstrated an ambipolar phosphorene field effect transistor with record high electron mobility. We also extracted the contact resistance values in our Schottky barrier phosphorene FETs and comprehensively discussed its effects on the device performance. We proposed and implemented a novel technique of extracting the Schottky barrier height and the transport gap of an ultrathin body semiconductor like phosphorene from the field effect characteristics of a transistor. Finally, we demonstrate a fully complementary inverter based on ambipolar phosphorene FETs.

## METHODS

Phosphorene flakes obtained from smart elements (<http://www.smart-elements.com/>) were mechanically exfoliated on 20 nm thick  $\text{SiO}_2$  layers on highly doped Si substrates used as

the back gate. The use of 20 nm thick  $\text{SiO}_2$  compared to conventionally used 300 nm thick  $\text{SiO}_2$  was motivated by the fact that scaled oxide reduces the Schottky barrier tunneling distance and thereby improves the carrier injection.<sup>28,29</sup> Since thin phosphorene layers are highly unstable in air, immediately



after the exfoliation, the substrate was transferred into a high vacuum electron-beam evaporator to deposit a 10 nm thick layer of alumina ( $\text{Al}_2\text{O}_3$ ). Note that the presence of a transparent  $\text{Al}_2\text{O}_3$  film does not prevent optical identification of thin flakes under the microscope. Figure 1a shows the AFM image of a 1.9 nm thick flake with the  $\text{Al}_2\text{O}_3$  coating on top. Next electron-beam lithography was used to pattern the source/drain contact electrodes. Right before the metal deposition, the  $\text{Al}_2\text{O}_3$  layer was removed from the contact area by submerging the sample in MF26A developer for 20 s, which does not react with phosphorene (see Supporting Information). The 70 nm thick titanium was used as the contact metal. Use of low work function metal such as Ti compared to high work function metals such as Ni, Au, or Pd reduces the Schottky barrier height for electron injection and thereby facilitates electron transport. Finally, atomic layer deposition (ALD) was used to deposit an additional 50 nm thick  $\text{Al}_2\text{O}_3$  film on top of the existing 10 nm  $\text{Al}_2\text{O}_3$ . The ALD was performed at 240 °C using alternating exposures of trimethylaluminum  $\text{Al}(\text{CH}_3)_3$  and  $\text{H}_2\text{O}$ . The presence of a 10 nm buffer layer of  $\text{Al}_2\text{O}_3$  prevents the reaction of water with phosphorene during the initial growth cycles of  $\text{Al}_2\text{O}_3$ . The total capping layer thickness was 60 nm.

**Conflict of Interest:** The authors declare no competing financial interest.

**Acknowledgment.** The work of S.D. is supported by the DOE Office of High Energy Physics under DoE Contract No. DE-AC02-06CH11357. Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

**Supporting Information Available:** More information on the effect of MF26A developer on phosphorene flakes and hysteresis in the phosphorene devices is provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- Geim, A. K.; Novoselov, S. K. The Rise of Graphene. *Nat. Mater.* **2007**, *6*, 183–191.
- Palacios, T. Graphene Electronics: Thinking Outside the Silicon Box. *Nat. Nanotechnol.* **2011**, *6*, 464–465.
- Jiao, L.; Zhang, L.; Wang, X.; Diankov, G.; Dai, H. Narrow Graphene Nano-ribbon from Carbon Nanotubes. *Nature* **2009**, *438*, 877–880.
- Zhang, Y.; Tang, T.; Girit, C.; Hao, Z.; Martin, M. C.; Zettl, A.; Crommie, M. F.; Shen, Y. R.; Wang, F. Direct Observation of Widely Tunable Bandgap in Bi-layer Graphene. *Nature* **2009**, *459*, 820–823.
- Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-Layer  $\text{MoS}_2$  Transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150.
- Das, S.; Appenzeller, J. Screening and Interlayer Coupling in Multilayer  $\text{MoS}_2$ . *Phys. Status Solidi RRL* **2013**, *7*, 268–273.
- Wang, H.; Yu, L.; Lee, Y.; Shi, Y.; Hsu, A.; Chin, M. L.; Li, L.; Dubey, M.; Kong, J.; Palacios, T. Integrated Circuits Based on Bi-layer  $\text{MoS}_2$  Transistors. *Nano Lett.* **2012**, *12*, 4674–4680.
- Das, S.; Gulotty, R.; Sumant, A.; Roelofs, A. All Two-Dimensional, Flexible, Transparent, and Thinnest Thin Film Transistors. *Nano Lett.* **2014**, *14*, 2861–2866.
- Podzorov, V.; Garshenson, M. E.; Kloc, Ch.; Zeis, R.; Bucher, E. High-Mobility Field-Effect Transistors Based on Transition Metal Dichalcogenides. *Appl. Phys. Lett.* **2004**, *84*, 3301.
- Das, S.; Appenzeller, J.  $\text{WSe}_2$  Field Effect Transistors with Enhanced Ambipolar Characteristics. *Appl. Phys. Lett.* **2013**, *103*, 103501.
- Pradhan, N. R.; Rhodes, D.; Feng, S.; Xin, Y.; Memaran, S.; Moon, H. B.; Terrones, H.; Terrones, M.; Balicas, L. Field Effect Transistor Based on Few-Layered  $\alpha$ - $\text{MoTe}_2$ . *ACS Nano* **2014**, *8*, 5911–5920.
- Lin, Y. F.; Xu, Y.; Wang, S.; Li, S.; Yamamoto, M.; Ferreira, A. A.; Li, W.; Sun, H.; Nakaharai, S.; Jian, W. B.; et al. Ambipolar  $\text{MoTe}_2$  Transistors and Their Applications in Logic Circuits. *Adv. Mater.* **2014**, *26*, 3263–3269.
- Hwang, W. S.; Remskar, M.; Yan, R.; Protasenko, V.; Tahy, K.; Chae, S. D.; Zhao, P.; Konar, A.; Xing, H.; Seabaugh, A.; et al. Transistors with Chemically Synthesized Layered Semiconductor  $\text{WS}_2$  Exhibiting  $10^5$  Room Temperature Modulation and Ambipolar Behavior. *Appl. Phys. Lett.* **2012**, *101*, 013107.
- Fang, H.; Chuang, S.; Chang, T. C.; Takei, K.; Takahashi, T.; Javey, A. High-Performance Single Layered  $\text{WSe}_2$  p-FETs with Chemically Doped Contacts. *Nano Lett.* **2012**, *12*, 3788–3792.
- Larentis, S.; Fallahazad, B.; Tutuc, E. Field-Effect Transistors and Intrinsic Mobility in Ultra-thin  $\text{MoSe}_2$  Layers. *Appl. Phys. Lett.* **2012**, *101*, 223104.
- Liu, L.; Balakumar, S.; Ouyang, Y.; Guo, J. Performance Limits of Monolayer Transition Metal Dichalcogenide Transistors. *IEEE Trans. Electron Devices* **2011**, *58*, 3042–3047.
- Das, S.; Appenzeller, J. Evaluating the Scalability of Multi-layer  $\text{MoS}_2$  FETs. *Device Res. Conf.* **2013**, 153–154.
- Liu, H.; Neal, A. T.; Ye, P. Channel Length Scaling of  $\text{MoS}_2$  MOSFETs. *ACS Nano* **2012**, *6*, 8563–8569.
- Das, S.; Appenzeller, J. Where Does the Current Flow in Two-Dimensional Layered Systems? *Nano Lett.* **2013**, *13*, 3396–3402.
- Li, L.; Yu, Y.; Ye, G. J.; Ge, Q.; Ou, X.; Wu, H.; Feng, D.; Chen, X. H.; Zhang, Y. Black Phosphorous Field Effect Transistor. *Nat. Nanotechnol.* **2014**, *9*, 372–377.
- Liu, H.; Neal, A. T.; Zhu, Z.; Xu, X.; Tomanek, D.; Ye, P. D. Phosphorene: An Unexplored 2D Semiconductor with High Hole Mobility. *ACS Nano* **2014**, *8*, 4033–4041.
- Das, S.; Zhang, W.; Dubey, M.; Demarteau, M.; Hoffmann, A.; Roelofs, A. Tunable Transport Gap in Phosphorene. *Nano Lett.* **2014**, *14*, 5733–5739.
- Liu, H.; Neal, A. T.; Mengwei, S.; Du, Y.; Ye, P. The Effect of Dielectric Capping on Few-Layer Phosphorene Transistors: Tuning the Schottky Barrier Heights. *IEEE Electron Device Lett.* **2014**, *35*, 795–797.
- Du, Y.; Liu, H.; Deng, Y.; Ye, P. Device Perspective for Black Phosphorus Field-Effect Transistors: Contact Resistance, Ambipolar and Scaling. *arXiv:1408.4206* **2014**.
- Kappera, R.; Voiry, D.; Ebru, S.; Branch, B.; Gupta, G.; Mohite, A. D.; Chhowalla, M. Phase-Engineered Low-Resistance Contacts for Ultrathin  $\text{MoS}_2$  Transistors. *Nat. Mater.* **2014**, *10*, 1038/nmat4080.
- Chuang, S.; Battaglia, C.; Azcatl, A.; McDonnell, S.; Kang, J. S.; Yin, X.; Tosun, M.; Kapadia, R.; Fang, H.; Wallace, R.; et al.  $\text{MoS}_2$  p-Type Transistors and Diodes Enabled by High Work Function  $\text{MoO}_x$  Contacts. *Nano Lett.* **2014**, *14*, 1337–1342.
- Gong, C.; Colombo, L.; Wallace, R.; Cho, K. J. The Unusual Mechanism of Partial Fermi Level Pinning at Metal  $\text{MoS}_2$  Interfaces. *Nano Lett.* **2014**, *14*, 1714–1720.
- Das, S.; Prakash, A.; Salazar, R.; Appenzeller, J. Toward Low Power Electronics: Tunneling Phenomena in TMDs. *ACS Nano* **2014**, *8*, 1681–1689.
- Yan, R. H. Scaling of Si MOSFET: From Bulk to SOI to Bulk. *IEEE Trans. Electron Devices* **1992**, *39*, 1704–1710.
- Lundstrom, M. *Nanoscale Transistors: Device Physics, Modeling and Simulation*; Springer: Berlin, 2006.
- Datta, S. *Quantum Transport: Atom to Transistor*; Cambridge University Press: Cambridge, 2005.
- Xia, J.; Chen, F.; Li, J.; Tao, N. Measurement of the Quantum Capacitance of Graphene. *Nat. Nanotechnol.* **2009**, *4*, 505–509.
- Zhang, S.; Yang, J.; Xu, R.; Wang, F.; Li, W.; Ghufran, M.; Zhang, Y. W.; Yu, Z.; Zhang, G.; Qin, Q.; et al. Extraordinary Photoluminescence and Strong Temperature/Angle-Dependent Raman Responses in Few-Layer Phosphorene. *ACS Nano* **2014**, *8*, 9590–9596.